# PLASMA CONDITIONS IN A MOLY-OXIDE ELECTRODELESS BULB DISCHARGE*

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*Abstract*

A mercury-free, molybdenum-oxide, electrodeless discharge is describe with potential application to lighting. A spectrum is presented which displays emission in the near UV and throughout the visible region. Plasma diagnostics using spectroscopy and interferometry are presented to obtain the electron temperature and density. The Mo density is estimated from an actinometry approach including a collisional radiative model of the plasma. The low pressure metallic plasma is a non-equilibrium discharge with ~40 lumens per watt.

## I. INTRODUCTION

Due to the potential for environmental regulations, there has recently been substantial interest in non-mercury plasma discharges for lighting applications. In the standard low pressure fluorescent bulb, xenon [1] or pulsed xenon-neon mixtures are under investigation as replacements for Hg [2]. Such rare gas fills require new phosphors and affect the electrode behavior [2,3]. In high pressure discharges metallic zinc has been studied as a mercury replacement as it is also a group IIB element in the periodic table [4]. Very high bulb temperatures (~1500K) are needed to volatize the zinc. Among electrodeless systems, the sulfur lamp [5,6] and the cluster lamp, composed of oxi-halides [7,8], provide Hg free visible light by microwave generation.

On board US Navy vessels Hg is already treated as hazardous material. Spent fluorescent bulbs must be stored at sea which consumes precious cargo space. The Naval Research Laboratory is presently investigating an electrodeless molybdenum-oxide discharge for high intensity lighting applications [9]. The concept is similar to a metal-halide lamp except that oxygen takes the place of the halide, no Hg is involved, and it is run at a low pressure. The volatile properties of metal-oxides has also been employed in a high intensity, high pressure NbO lamp as discussed by Lapatovich, et al. [10,11], but their device includes Hg. The present paper contains a brief discussion of the moly-oxide Hg-free lamp operation and presents measurements of fundamental discharge parameters, including electron density from interferometry, electron temperature from near infrared (nir) emission lines, and Mo atom density from actinometry.

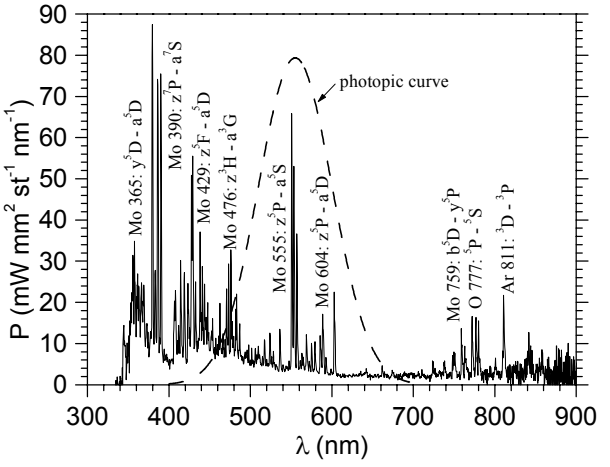


**Figure 1.** Calibrated spectrum from a moly-oxide electrodeless discharge with Ar. The photopic curve is the eye sensitivity.

## II. EXPERIMENTAL SETUP

The experiments were performed using quartz bulbs of inner diameter ~2.3 cm, each with a long, narrow (0.4 cm diameter), tubular neck which was connected to a pumping system. A quartz rod extended through the neck into the bulb, where it flared outward to a diameter larger than the neck. The bulb could be mechanically closed or opened by moving the rod through a vacuum connection. The discharge was operated as follows. A charge of $MoO_3$ is introduced into the bulb as a powder. After the neck is attached to the vacuum system a weak Ar discharge is run and then the bulb is pumped down to ~$10^{-5}$ Torr in order to remove contaminants such as water. The bulb is backfilled with Ar between 0.5 and 8 Torr and closed using the flared rod. An inductive discharge is initiated in the Ar buffer via a 2 μH spiral coil driven by a 13.56 MHz

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14. ABSTRACT
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RF generator. An automatic dual capacitor network is used for proper matching. Since the vapor pressure of $MoO_3$ is 1 Torr at 1007 K and 20 Torr at 1058 K, the moly-oxide undergoes a sudden evaporation from the quartz walls as they heat up. Once in the plasma kinetic reactions dissociate the $MoO_3$. The Mo atom, and possibly MoO, are excited by electron collisions and radiate in the near UV and throughout the visible domain.

A sample spectrum is shown in Fig.1. The data was taken with an Ocean Optics model PC2000 spectrometer. The bulb image is focused through a 1:1 optics system onto a fiber optic and recorded on a computer. The raw data count has been absolutely calibrated for the spectral response of the optics train using the OL550 standard of spectral radiance from Optronic Laboratories. The identification of the prominent emission lines and the term designations in the spectrum of Fig.1 are taken from the list of Whaling, et al. [12]. The resonant transitions of MoI occur from the $z^7$ level near 390 nm to ground level ($a^7S$). Most of the visible emission lines are between quintet states ($z^5$ to $a^5$). Thus the relevant excitation path is from the ground state to a septet state, followed by a collisional exchange to a quintet level, and then a radiative decay leading to visible emission. The photopic response function, which represents the sensitivity of the human eye, is represented in the figure as the dashed line. Note that the Mo 555 line is located very near the peak of the eye sensitivity. The electrical power input for this discharge was 250 W and the total lumen output was ~10000 lm.

## III. PLASMA PROPERTIES

The electron density, $n_e$, was measured using a microwave interferometer at 140 GHz. The transmitting leg of the interferometer circuit included focusing horns and a variable attenuator. The reference leg had a variable phase shifter as well as an attenuator. The two signals were combined in a short slot hybrid coupler and two crystal detectors from Millitech (DXP-08) were used to monitor the signals. The non-linear response of each detector was calibrated with a power meter following the procedure of Hotston and Seidl [13]. The measurements were made by interrupting the RF while triggering the oscilloscope to record the detector signals as the plasma decayed. The approach of Lindberg and Eriksson [14] was adopted to treat phase changes greater than $\pi$.

Results for $n_e$ as a function of power are presented in Fig.2. For these experiments the pre-discharge Ar pressure was set at 1 Torr. In the pure Ar discharge the electron density increases with power, but in the moly-oxide discharge the opposite occurs. This decrease in $n_e$ reflects the increase in the gas phase density of Mo. As the Mo density increases more of the input power is channeled into Mo atomic excitations and the energy cost per electron-ion pair, $\theta$, increases dramatically. Consequently, the radiative emission should increase and we find that the total visible output for the points with $n_e$~$2x10^{13}$ $cm^{-3}$ is ~10 times larger than for the lower

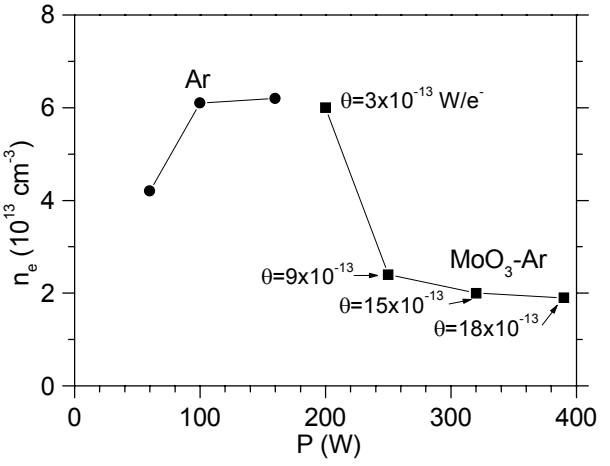


**Figure 2.** Electron density as a function of input electrical power for pure Ar (circles) and for $MoO_3$-Ar (squares) discharges. The power per electron-ion pair is denoted for the latter set.

power point with $n_e$~$6x10^{13}$. The spectrum for the point at ~240 W is similar to that shown in Fig.1.

Spectroscopy in the nir region was performed to determine the electron temperature, $T_e$. The optical configuration was similar to that discussed in Section II but a nir fiber and spectrometer from Ocean Optics were chosen to resolve the 700-900 nm spectral region. This domain contains many Ar emission lines from the ten 2p to the four 1s Paschen levels. Again absolute intensities were obtained after correction for the spectral response function. The observations were compared with synthetic spectra of Ar emission calculated with a collisional radiative population dynamics model. At the relatively high electron densities determined above, the model indicated that the absolute Ar intensities were strongly dependent on $T_e$, but only weakly on $n_e$. This is because the collisional excitation to the 2p states from the ground and 1s states is balanced primarily by ionization to $Ar^+$, and three-body recombination is not important. In steady state $n_e$ can then be eliminated from the rate equations. The energy separations among the 2p levels and the ground state means that absolute intensities vary by over four orders of magnitude between $T_e$ = 0.5 and 2 eV.

The measurement of $T_e$ as a function of pressure is shown in Fig.3, For these experiments the bulb was not closed off allowing a simultaneous measurement of the plasma pressure. The decrease in $T_e$ from ~1.5 to ~1 eV with pressure follows the general trend for a discharge wherein the electron loss is diffusion-controlled [15]. The small difference between the pure Ar case and that with moly-oxide was due to i) the small charge of $MoO_3$ used in these experiments, ii) the low coupled power (150 W), and iii) the loss of Mo by diffusion to the colder neck portion of the open bulb. In the closed bulb configuration we expect $T_e$ to be somewhat lower since the Ar emission lines from the 2p to 1s levels are observed to be weaker in intensity.

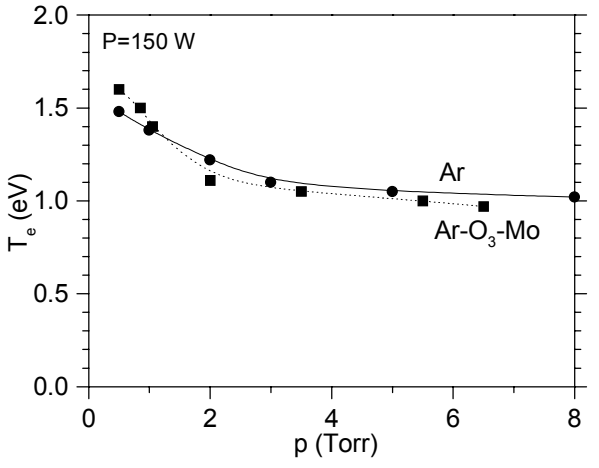


**Figure 3.** Electron temperature as a function of pressure for pure Ar (circles) and for a moly-oxide-Ar discharge (squares).

## IV. Mo DENSITY

One of the key properties of the moly-oxide discharge is the number density of Mo atoms, $n_{Mo}$. The measurement of electron density in Fig.2 suggests that $n_{Mo}$ increases with power with the consequence of significantly enhanced visible emission. To estimate $n_{Mo}$ we employ a variation of the standard actinometry method by comparing observed emission line ratios from Mo, Ar, and O with synthetic spectra from a model including all of these species. In this model we calculated the electron energy distribution function by solving the time-independent homogeneous electron Boltzmann equation, using the conventional two-term expansion in Legendre polynomials. Two lumped excited states of Mo are included in the kinetic model, vis., the resonance levels $Mo(y^7+z^7)$ and the dominant optically emitting levels $Mo(y^5+z^5)$. The electronic structure of neutral Mo is extremely complex containing about 2000 energy levels. The present crude model focuses on the excitation and emission path discussed at the end of Section II. For the oxygen atom four excited states are considered: the two metastable states $^1S$ and $^1D$ and two groups of levels, namely 3s and 3p. The dominant specie is argon and various levels, treated as blocks of levels, are used in the model. These are: Ar(n*s*) (n=4,5,6), Ar(n*p*) (n=4,5) and Ar(n*d*) (n=3,4). Excited states of $O_2$ were not taken into account; however, various processes involving ground state of $O_2$ are considered, such as vibrational and electronic excitation, dissociation and attachment. The ionized species $Ar^+$, $Ar_2^+$, $Mo^+$, $O^+$, $O_2^+$, O and $O_2^-$, were included in their ground states. The populations were determined with a collisional radiative model along with a probability-of-escape treatment for the radiation. At a fixed Ar pressure and input power, the Mo pressure was varied (keeping $p_{O2}=1.5p_{Mo}$), and Mo, O and Ar line intensities are calculated.

Figure 4 displays the ratio of O 777nm and several Mo lines to the Ar 811nm line at different Mo pressures. The discharge parameters are 250 W coupled power and 1 Torr initial Ar pressure. The measured ratios of the same line intensities are taken from the experiment with $\theta=9x10^{-13}$ W/e$^-$ in Fig.2. The comparison indicates that the partial pressure of Mo is between 2 and 4 mTorr.

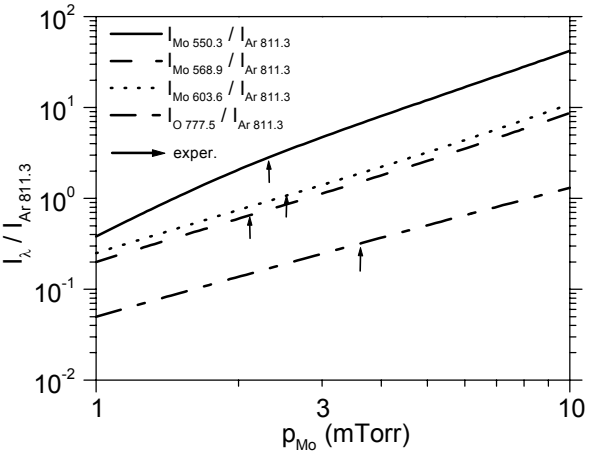


**Figure 4.** Comparison of line intensities from Mo and O with Ar as a function of the Mo partial pressure. The lines are from model calculations and the arrows denote experimental values for the line intensity ratios.

## V. DISCUSSION

We have presented diagnostic results for the electron density, electron temperature, and molybdenum partial pressure in an electrodeless moly-oxide-argon discharge. This discharge has potential applications as a Hg-free, compact light source. Fig.1 indicates that metallic emission is the dominant contributor to the visible light. The same property is true for high pressure metal halide lamps, but the plasma conditions are quite different. The present moly-oxide discharge operates at low pressure (few Torr) and the measured electron temperature is ~1 eV from Fig.3. Though we have no measurement of the central gas temperature $T_g$, theoretical estimates of the energy transfer from electrons to the gas suggest it is of order 1500 to 2000 K. Thus $T_e >> T_g$, and the plasma is not in equilibrium as it is in the metal-halide discharges. Non-equilibrium discharges containing metals with open nd- and (n+1)s-shells, such as Mo, are a challenge to model due to the large number of energy levels. The approach taken here was limited to the Mo excitation path leading to emission near 550 nm. In combination with actinometry we estimate a few mTorr partial pressure for Mo. Improvements to the model would require more (lumped) states along with excitation cross-sections.

The present moly-oxide discharge has attained an efficacy of 40 lumens per watt, similar to the Hg-NbO of

Ref.[11]. For use in general lighting, the efficiency could be increased by converting the near UV emission seen in Fig.1 to visible light through a phosphor. An alternative approach would be an increase in the Mo density or the addition of other absorbing metals in the discharge such that the UV resonance lines become optically thick. This could enhance the transitions in the visible region of the spectrum relative to the UV component.

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